

AN APPLICATION OF HIRSCHFELDER-SILBEY PERTURBATION THEORY TO THE H_2^+ ION*

by

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The Hirschfelder-Silbey perturbation theory⁽¹⁾ has been applied to the H_2^+ molecular ion. The first order perturbation equation has been solved by means of a variational method and the resulting gerade and ungerade energies are given through third order.

The ungerade energy is in very good agreement with the exact energy, but the corresponding gerade energy is relatively poor. These results are currently under investigation.

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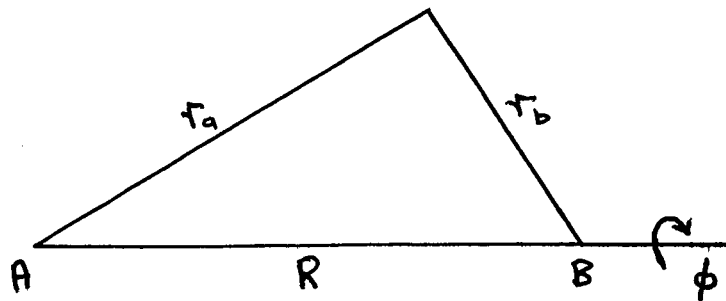


figure 1

Substituting equations (2) into (1) and adding the resulting equations gives

$$H a = \left(\frac{E_g + E_u}{2} \right) a + \left(\frac{E_g - E_u}{2} \right) b \quad (3)$$

which is the equation we wish to solve by perturbation methods.

We write

$$a = a^{(0)} + a^{(1)} + a^{(2)} + \dots$$

$$b = b^{(0)} + b^{(1)} + b^{(2)} + \dots$$

$$E_g = E_g^{(0)} + E_g^{(1)} + E_g^{(2)} + \dots$$

$$E_u = E_u^{(0)} + E_u^{(1)} + E_u^{(2)} + \dots$$

$$H = H_a + V_a = H_b + V_b$$

where

$$H_a = -\frac{1}{2} \nabla^2 - \frac{1}{r_a}$$

$$H_b = -\frac{1}{2} \nabla^2 - \frac{1}{r_b}$$

$$V_a = -1/r_b$$

$$V_b = -1/r_a$$

Substituting these expressions into (3) and equating terms of like order we obtain the set of perturbation equations.

$$H_a a^{(0)} = \epsilon^{(0)} a^{(0)}$$

$$H_a a^{(1)} + V_a a^{(0)} = \epsilon^{(0)} a^{(1)} + \sigma^{(1)} a^{(0)} + \Delta^{(1)} b^{(0)} \quad (4)$$

$$H_a a^{(2)} + V_a a^{(1)} = \epsilon^{(0)} a^{(2)} + \sigma^{(1)} a^{(1)} + \sigma^{(2)} a^{(0)} \\ + \Delta^{(1)} b^{(1)} + \Delta^{(2)} b^{(0)}$$

where $\sigma^{(i)} = \frac{\epsilon_g^{(i)} + \epsilon_u^{(i)}}{2}$, $\Delta^{(i)} = \frac{\epsilon_g^{(i)} - \epsilon_u^{(i)}}{2}$

H_a is the Hamiltonian of a hydrogen atom centred on A and we choose $a^{(0)}$ to be the ground state eigenfunctions of the hydrogen atom; $\epsilon^{(0)}$ is hence the ground state energy of the hydrogen atom ($= -0.5$ a.u.)

A knowledge of ψ_g and ψ_u through nth order determines the energy through $(2n+1)$ st order. So we require

$$\epsilon_{(g)}^{(0)} = \frac{\langle \psi_{(g)}^{(0)} | H | \psi_{(g)}^{(0)} \rangle}{\langle \psi_{(g)}^{(0)} | \psi_{(g)}^{(0)} \rangle} = \epsilon^{(0)} + \epsilon_{(g)}^{(1)}$$

$$\epsilon_{(g)}^{(1)} = \frac{\langle \psi_{(g)}^{(0)} + \psi_{(g)}^{(1)} | H | \psi_{(g)}^{(0)} + \psi_{(g)}^{(1)} \rangle}{\langle \psi_{(g)}^{(0)} + \psi_{(g)}^{(1)} | \psi_{(g)}^{(0)} + \psi_{(g)}^{(1)} \rangle}$$

$$= \epsilon^{(0)} + \epsilon_{(3)}^{(1)} + \frac{(\epsilon_{(3)}^{(2)} + \epsilon_{(3)}^{(3)}) \langle \psi_{(3)}^{(0)} | \psi_{(3)}^{(0)} \rangle + 2 \epsilon_{(3)}^{(2)} \langle \psi_{(3)}^{(0)} | \psi_{(3)}^{(1)} \rangle}{\langle |\psi_{(3)}^{(0)} + \psi_{(3)}^{(1)}|^2 \rangle}$$

which means that we have

$$\langle b^{(0)} | H_a - \epsilon^{(0)} | a^{(1)} \rangle = 0$$

$$\langle b^{(0)} | H_a - \epsilon^{(0)} | a^{(2)} \rangle = 0$$

for the exact $a^{(1)}$ and $a^{(2)}$. Note that we do not require $\psi_{(3)}^{(0)}$ to be normalized or orthogonal to higher order wave functions. i.e.

$$\langle \psi_{(3)}^{(0)} | \psi_{(3)}^{(0)} \rangle \neq 1 \quad \text{and} \quad \langle \psi_{(3)}^{(0)} | \psi_{(3)}^{(1)} \rangle \neq 0$$

Also from the above relationships we obtain the following expressions for the energy terms up to third order.

$$\epsilon_{(3)}^{(1)} \langle a^{(0)} | a^{(0)} \pm b^{(0)} \rangle = \langle a^{(0)} | V_a | a^{(0)} \rangle \pm \langle a^{(0)} | V_a | b^{(0)} \rangle \quad (5)$$

$$\begin{aligned} \epsilon_{(3)}^{(2)} \langle a^{(0)} | a^{(0)} \pm b^{(0)} \rangle &= 2 \langle a^{(0)} | V_a | a^{(1)} \rangle \pm 2 \langle a^{(0)} | V_a | b^{(1)} \rangle \\ &\quad - 2 \epsilon_{(3)}^{(1)} \langle a^{(0)} | a^{(1)} \pm b^{(1)} \rangle \\ &\quad + \langle a^{(1)} | H_a - \epsilon^{(0)} | a^{(1)} \rangle \\ &\quad \pm \langle a^{(1)} | H_a - \epsilon^{(0)} | b^{(1)} \rangle \end{aligned} \quad (6)$$

$$\begin{aligned}
\epsilon_{(g)}^{(3)} \langle a^{(0)} | a^{(0)} \pm b^{(0)} \rangle &= \langle a^{(1)} | V_a | a^{(0)} \rangle \pm \langle a^{(1)} | V_a | b^{(0)} \rangle \\
&- \epsilon_{(g)}^{(1)} \langle a^{(1)} | a^{(1)} \pm b^{(1)} \rangle \\
&- 2 \epsilon_{(g)}^{(2)} \langle a^{(1)} | a^{(0)} \pm b^{(0)} \rangle
\end{aligned} \tag{7}$$

It should be noted that when the exact $a^{(1)}$ is known the expression (6) for $\epsilon_{(g)}^{(2)}$ can be reduced, using the 1st order equation (4), to

$$\begin{aligned}
\epsilon_{(g)}^{(2)} \langle a^{(0)} | a^{(0)} \pm b^{(0)} \rangle &= \langle a^{(0)} | V_a | a^{(1)} \rangle \pm \langle a^{(0)} | V_a | b^{(1)} \rangle \\
&- \epsilon_{(g)}^{(1)} \langle a^{(0)} | a^{(1)} \pm b^{(1)} \rangle
\end{aligned}$$

However, when solving for $a^{(1)}$ by a variational method we are not working with the exact $a^{(1)}$ so (6) should be used to obtain

Solution of the first order equation by a variation method

If we construct the functional

$$\begin{aligned}
J &= \langle X | H_a - \epsilon^{(0)} | X \rangle + \langle X | V_a - \epsilon_g^{(1)} | a^{(0)} \rangle \\
&+ \langle a^{(0)} | V_a - \epsilon_g^{(1)} | X \rangle - \Delta^{(1)} \langle X | b^{(0)} - a^{(0)} \rangle \\
&- \Delta^{(1)} \langle b^{(0)} - a^{(0)} | X \rangle
\end{aligned}$$

we see that when J is stationary with respect to first order variations of X then X is a solution of the first order equation (4).

If we expand χ in a complete set of functions

$$\chi = \sum_n c_n \psi_n \quad (8)$$

then

$$\begin{aligned} J &= \sum_{n,m} c_n c_m \langle \psi_n | H_a - \epsilon^{(0)} | \psi_m \rangle \\ &\quad + 2 \sum_n c_n \langle \psi_n | V_a - \epsilon_g^{(1)} | a^{(0)} \rangle \\ &\quad - 2 \Delta^{(1)} \sum_n c_n \langle \psi_n | b^{(0)} - a^{(0)} \rangle \\ &= \sum_{n,m} c_n c_m H_{nm} + 2 \sum_n c_n V_n \end{aligned}$$

where

$$\begin{aligned} H_{nm} &= \langle \psi_n | H_a - \epsilon^{(0)} | \psi_m \rangle \\ V_n &= \langle \psi_n | (V_a - \epsilon_g^{(1)}) a^{(0)} \\ &\quad - \Delta^{(1)} (b^{(0)} - a^{(0)}) \rangle \end{aligned} \quad (9)$$

We require J to be stationary w.r.t. changes in the C 's

$$\begin{aligned} \text{i.e. } \frac{\partial J}{\partial c_\ell} = 0 &= \sum_n' c_n H_{n\ell} + \sum_m c_m H_{\ell m} \\ &\quad + 2 c_\ell H_{\ell\ell} + 2 V_\ell \end{aligned}$$

The prime indicates that the $n = \ell$ term is omitted from the summation.

Since $H_{n\ell} = H_{\ell n}$ we have

$$2 \sum c_n H_{n\ell} + 2V_\ell = 0 \quad (10)$$

In general we need

$$\frac{\partial J}{\partial c_1} = \frac{\partial J}{\partial c_2} = \dots = \frac{\partial J}{\partial c_\ell} = \dots = 0$$

which gives an infinite set of equations of the form (10). If we consider only a finite number of basis functions in the expansion (8) for χ i.e. write

$$\chi = \sum_{n=1}^N c_n \psi_n$$

then the set of N equations (10) may be written as

$$\begin{pmatrix} H_{11} & H_{12} & \dots & H_{1N} \\ H_{21} & H_{22} & \dots & H_{2N} \\ \dots & \dots & \dots & \dots \\ H_{N1} & H_{N2} & \dots & H_{NN} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} = - \begin{pmatrix} V_1 \\ V_2 \\ \vdots \\ V_N \end{pmatrix}$$

That is

$$H \mathbf{c} = -\mathbf{V}$$

$$\text{so } \mathbf{c} = -H^{-1} \mathbf{V} \quad (11)$$

For a given basis set the matrices H and \mathbf{V} may be obtained and hence \mathbf{c} is derived by the usual matrix inversion techniques.

The set of basis functions used were the Löwdin orbitals⁽²⁾ which have the general form

$$\psi_{nlm} = R_{nl}(\tau) Y_l^m(\theta, \phi)$$

where

$$R_{nl}(\tau) = \frac{2^{3/2}}{(n+l+1)!} \left\{ \frac{(n-l-1)!}{(n+l+1)!} \right\}^{1/2} (2\tau)^l L_{n+l+1}^{2l+2}(2\tau) e^{-\tau} \quad (12)$$

and $Y_l^m(\theta, \phi)$ are the usual surface harmonics and L_{n+l+1}^{2l+2} are the Laguerre polynomials,

This set of functions appear superficially to be similar to the hydrogenic functions however they have only one function in common, that is the ground state $1s$ hydrogen eigenfunction. The advantage gained by using the Löwdin orbitals is that a denumerably infinite set of them is complete, whereas the hydrogenic orbitals form a complete set only when continuum states are included. It is hoped that an expansion in terms of Löwdin orbitals will converge to the solution for $a^{(1)}$ more rapidly than an expansion of hydrogenic orbitals would.

From an examination of the first order equation

$$(H_a - \epsilon^{(0)}) a^{(1)} - \frac{1}{r_b} a^{(0)} = \sigma^{(1)} a^{(0)} + \Delta^{(1)} b^{(0)} \quad (13)$$

we see that the equation has a pole at $r_b = 0$; we therefore expect a singularity in the solution at $r_b = 0$.

Now near $r_b = 0$ the second term in (13) has the form

$$-\frac{1}{r_b} e^{-R}$$

since $r_a = R$ at r_b . If we write

$$a^{(1)} = c_1 e^{-R} b^{(0)} + \dots$$

$$H_a a^{(1)} = c_1 e^{-R} H_a b^{(0)} + \dots$$

$$= c_1 e^{-R} \left(T - \frac{1}{r_a} \right) b^{(0)} + \dots$$

$$= c_1 e^{-R} \left(H_b + \frac{1}{r_b} - \frac{1}{r_a} \right) b^{(0)} + \dots$$

$$= c_1 e^{-R} \left(\epsilon^{(0)} + \frac{1}{r_b} - \frac{1}{r_a} \right) b^{(0)} + \dots$$

$$\therefore (H_a - \epsilon^{(0)}) a^{(1)} = c_1 e^{-R} \left(\frac{1}{r_b} - \frac{1}{r_a} \right) b^{(0)} + \dots$$

So at $r_b \approx 0$

$$(H_a - \epsilon^{(0)}) a^{(1)} \sim c_1 e^{-R} \frac{1}{r_b} b^{(0)}$$

So introduction of a term of the form $c_1 e^{-R} b^{(0)}$ in $a^{(1)}$ will remove the singularity at $r_b = 0$.

In the light of this the trial $a^{(1)}$ was constructed from a linear combination of $e^{-R} b^{(0)}$ with a finite set of Lwdin orbitals. The finite set chosen did not include the $1s$ orbital hence each term in the set was orthogonal to $a^{(0)}$. In order to solve (11) for the matrix

Ⓒ it is necessary first to have the matrix elements H_{nm} and V_n .

The H_{nm} elements may be obtained directly from the work of Hirschfelder and Löwdin⁽³⁾. We have,

$$\langle \psi_{nl} | H_a - \epsilon^{(0)} | \psi_{nl} \rangle = \frac{4n-2l-1}{2(2l+3)} - \frac{1}{(l+1)} + \frac{1}{2}$$

$$\begin{aligned} \langle \psi_{nl} | H_a - \epsilon^{(0)} | \psi_{n'l'} \rangle &= \left\{ \frac{(n'+l+1)!}{(n'-l-1)!} \frac{(n-l-1)!}{(n+l+1)!} \right\}^{1/2} \delta_{ll'} \\ &\times \left[\frac{2n'+1}{2l+3} - \frac{1}{l+1} \right] : n > n' \end{aligned}$$

In the derivation of the elements V_n the functions have been written in terms of the prolate spheroidal coordinates defined by (see figure 1)

$$\xi = \frac{r_a + r_b}{R}, \quad \eta = \frac{r_a - r_b}{R}, \quad \phi$$

which gives

$$r_a = \frac{R}{2} (\xi + \eta)$$

$$r_b = \frac{R}{2} (\xi - \eta)$$

$$\cos \theta_a = \frac{(\xi \eta + 1)}{(\xi + \eta)}$$

$$\cos \theta_b = \frac{(\xi \eta - 1)}{(\xi - \eta)}$$

From (9) we have

$$V_{n'} = \langle \psi_{n'} | V_a | a^{(0)} \rangle - \epsilon_g^{(1)} \langle \psi_{n'} | a^{(0)} \rangle \\ - \Delta \langle \psi_{n'} | b^{(0)} \rangle + \Delta \langle \psi_{n'} | a^{(0)} \rangle$$

where the different n' refer to different values of n and l .

We can express the functions $\psi_{n'}$ in terms of spheroidal coordinates using the relations

$$L_{n+l+1}^{2l+2}(2r_{(g)}) = \sum_{p=0}^{n-l-1} c_p R^p(\xi \pm \eta)^p$$

$$P_l(\cos \theta_{(g)}) = \sum_{q=0}^l d_q \left(\frac{\xi \eta \pm 1}{\xi \pm \eta} \right)^q$$

where

$$c_p = \frac{(-1)^p [(n+l+1)!]^2}{(2l+2+p)! p! (n-l-p-1)!}$$

and

$$d_q = \frac{(-1)^{\left(\frac{l-q}{2}\right)} (l+q-1)!!}{(q)! 2^{\left(\frac{l-q}{2}\right)} \left(\frac{l-q}{2}\right)!} \delta_{l-q} ; \delta_{l-q} = 0, l-q \text{ odd} \\ = 1, l-q \text{ even}$$

When this is done we obtain expressions for

$$\langle \psi_{n'} | V_a | a^{(0)} \rangle, \langle \psi_n | a^{(0)} \rangle \text{ and } \langle \psi_n | b^{(0)} \rangle$$

which are given in the appendix.

Hence using these results H and V may be constructed and C found.

Once we have \mathcal{C} for some finite basis set of functions we can use the approximate $a^{(1)}$ they define to calculate the energies $E_{(a)}^{(2)}$, $E_{(a)}^{(3)}$ and $E_{(a)}(1)$. This has been done (making use of the integrals given in the appendix) for different sets of basis functions and some of the results are given in table 2.

Discussion of Results

We should note two points in connection with these results. First, although the variational method we are using to solve equation (4) will given an approximate $a^{(1)}$ which improves as basis functions are added successively, the expectation value of the Hamiltonian calculated using the wave function through first order (i.e. $E(1)$) will not necessarily decrease as each new basis function is added. That is the variation method does not systematically give a stationary value of $E(1)$.

The second point is that the second-order energy for the ungerade state, $E_u^{(2)}$, is positive in contrast to the results of the usual Rayleigh-Schrödinger theory where $E^{(2)} \leq 0$, always.

Suppose we take the original wave equation

$$H \psi_{(a)} = E_{(a)} \psi_{(a)}$$

and expand

$$H = H_a + V_a$$

$$E_{(a)} = E^{(0)'} + E_{(a)}^{(1)'} + E_{(a)}^{(2)'} + \dots$$

$$\psi_{(a)} = \psi_{(a)}^{(0)} + \psi_{(a)}^{(1)} + \psi_{(a)}^{(2)} + \dots$$

Using the first order wave function obtained by the 'new' perturbation theory as a trial wave function for a Rayleigh-Schrödinger treatment we obtain

$$\begin{aligned}
 \tilde{E}_{(a)}^{(2)'} &= \langle \tilde{\psi}_{(a)}^{(1)} | H_a - \epsilon^{(0)} | \tilde{\psi}_{(a)}^{(1)} \rangle + 2 \langle \tilde{\psi}_{(a)}^{(1)} | V_a | \psi_{(a)}^{(0)} \rangle \leq 0 \\
 &= \langle a^{(1)} | H_a - \epsilon^{(0)} | a^{(1)} \rangle \pm 2 \langle a^{(1)} | H_a - \epsilon^{(0)} | b^{(1)} \rangle \\
 &\quad + \langle b^{(1)} | H_a - \epsilon^{(0)} | b^{(1)} \rangle + 2 \langle a^{(1)} | V_a | a^{(0)} \rangle \\
 &\quad \pm 2 \langle a^{(1)} | V_a | b^{(0)} \rangle \pm 2 \langle b^{(1)} | V_a | a^{(0)} \rangle \\
 &\quad + 2 \langle b^{(1)} | V_a | b^{(0)} \rangle \leq 0
 \end{aligned}
 \tag{14}$$

If we take the second order energy given by the Hirschfelder-Silbey theory (6) and substitute in (14) we have

$$\begin{aligned}
 E_{(a)}^{(2)'} &= E_{(a)}^{(2)} \langle a^{(0)} | a^{(0)} \pm b^{(0)} \rangle + 2 E_{(a)}^{(1)} \langle a^{(0)} | a^{(1)} \pm b^{(1)} \rangle \\
 &\quad \pm \langle a^{(1)} | H_a - \epsilon^{(0)} | b^{(1)} \rangle + \langle b^{(1)} | H_a - \epsilon^{(0)} | b^{(1)} \rangle \\
 &\quad + 2 \langle b^{(0)} | V_a | b^{(1)} \rangle \pm 2 \langle b^{(0)} | V_a | a^{(1)} \rangle \leq 0
 \end{aligned}$$

This relationship does not appear to give any restrictions to the sign of $E_{(a)}^{(2)}$, so the positive values of $E_u^{(2)}$ need not be a cause for concern.

From an examination of Table 2 we see that using a basis of $e^{-R_b(0)}$ together with the 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5g Löwdin orbitals the ungerade energy $E_u(1)$ is very close to the 'exact' value given by Peek⁽⁴⁾.

However the gerade energy $\epsilon_g(1)$ compares relatively poorly with Peek's value and in fact we see that the basis set of 8 functions gave a better value for $\epsilon_g(1)$. It seems clear from these results that large basis sets should be used in an attempt to obtain convergence of $\epsilon_g(1)$ and $\epsilon_u(1)$ to some steady value. However, judging from the results we already have for the ungerade energy it would appear that the method is capable of giving fairly accurate results.

TABLE 1: Elements of Matrix \mathbb{C} for Different Numbers of Basis Functions for $R = 2$ a.u.

FUNCTIONS	1	2	3	4	5	6	7	8	9	10
$e^{-R} b_0$	0.5708	0.3463	0.3464	0.5255	0.7874	0.8268	0.8285	0.6821	0.8416	0.8743
2s	0.1956	0.1861	0.2529	0.2605	0.2716	0.2732	0.2733	0.2671	0.2739	0.2753
2p		0.0519	0.0519	-0.0037	-0.0245	0.0276	-0.0277	-0.0161	-0.0288	-0.0314
3s			-0.0946	-0.0946	-0.0946	-0.0819	-0.0819	-0.0828	-0.0818	-0.0816
3p				0.0949	0.0985	0.0990	0.0988	0.0983	0.0989	0.0900
3d				-0.0427	-0.0478	-0.0478	-0.0489	-0.0496	-0.0567	-0.0582
4s					-0.0163	-0.0163	-0.0164	-0.0152	-0.0165	-0.0167
4p							0.0004	-0.0021	0.0006	0.0016
4d								0.0326	0.0296	0.0291
4f									-0.0260	-0.0268
5g										-0.0105

TABLE 2: Energy Values for H_2^+ for $R = 2$ a.u.

No. of Basis Functions	$\epsilon_g^{(2)}$	$\epsilon_g^{(3)}$	$\Sigma_g^{(1)} + 1/R$	$\epsilon_u^{(2)}$	$\epsilon_u^{(3)}$	$\Sigma_u^{(1)} + 1/R$
1	-0.0394198	0.0090438	-0.5838431	0.0431470	-0.0220242	-0.1377550
2	-0.0440499	0.0084172	-0.5887618	0.0564354	-0.0157395	-0.1214032
3	-0.0497233	0.0206594	-0.5815299	0.0349909	-0.0181947	-0.1430619
4	-0.0608038	0.0187119	-0.5933887	0.0435494	-0.0395595	-0.1494156
5	-0.0599472	0.0213113	-0.5908069	0.0362460	-0.0479521	-0.1607079
6	-0.0606124	0.0200580	-0.5926965	0.0372752	-0.0505788	-0.1613713
7	-0.0606083	0.0200620	-0.5926943	0.0372589	-0.0506367	-0.1614198
8	-0.0612362	0.0185338	-0.5941077	0.0356335	-0.045500	-0.1597576
9	-0.0605262	0.0202197	-0.5922841	0.0308599	-0.0490240	-0.1659657
10	-0.0603320	0.0206194	-0.5918250	0.0297026	-0.0497634	-0.1674359
Exact ⁽⁴⁾	—	—	-0.6026342	—	—	-0.1675344

All energy values are in atomic units.

$$\epsilon^{(0)} = -0.5$$

$$\epsilon_g^{(1)} = -0.5537715$$

$$\epsilon_u^{(1)} = -0.1608540$$

$$\Sigma_g^{(0)} + 1/R = -0.5537715$$

$$\Sigma_u^{(0)} + 1/R = -0.1608540$$

Appendix

The following integrals are used in the solution of the matrix equation (11) and in the evaluation of the energy terms.

We define

$$K_{nl} = \frac{2^{3/2}}{(n+l+1)!} \left\{ \frac{(n-l-1)!}{(n+l+1)!} \frac{2l+1}{2} \right\}^{1/2}$$

$$\beta(N) = \frac{e^{-R}}{R^{N+1}} \sum_{i=0}^N \frac{N!}{(N-i)!} R^{N-i}$$

$$\gamma(N) = \frac{N!}{R^{N+1}} \sum_{i=0}^N \frac{R^{N-i}}{(N-i)!} \left\{ (-1)^{N-i} e^R - e^{-R} \right\}$$

$$\begin{aligned} \delta(N) &= \frac{2}{N+1} && : n \text{ even} \\ &= 0 && : n \text{ odd} \end{aligned}$$

R is the molecular bond length.

1.

$$\langle a^{(0)} | b^{(0)} \rangle = \frac{R^3}{4} \left\{ \beta(2) \delta(0) - \beta(0) \delta(2) \right\}$$

$$2. \quad \langle \psi_{ne}(a) | b^{(0)} \rangle$$

$$= \sqrt{2} K_{ne} \sum_{p=0}^{n-l-1} \sum_{q=0}^l c_p d_q \frac{R^{l+p+3}}{8} \sum_{s=0}^{l+p-q+1} \sum_{u=0}^q \binom{l+p-q+1}{s} \binom{q}{u} \\ \times [\beta(l+p-q-s+u+2) \delta(s+u) - \beta(l+p-q-s+u+1) \delta(s+u+1)]$$

$$3. \quad \langle \psi_{ne}(a) | \psi_{n'e'}(b) \rangle$$

$$= K_{ne} K_{n'e'} \sum_{p=0}^{n-l-1} \sum_{p'=0}^{n'-l'-1} \sum_{q=0}^l \sum_{q'=0}^{l'} c_p c_{p'} d_q d_{q'} \frac{R^{l+l'+p+p'+3}}{8} \\ \times \sum_{s=0}^{l+p-q+1} \sum_{s'=0}^{l'+p'-q'+1} \sum_{u=0}^q \sum_{u'=0}^{q'} \binom{l+p-q+1}{s} \binom{l'+p'-q'+1}{s'} \binom{q}{u} \binom{q'}{u'} \\ \times (-1)^{s'+q'+u'} \beta(l+l'+p+p'-q-q'-s-s'+u+u'+2) \delta(s+s'+u+u')$$

4.

$$\langle a^{(0)} | V_a | a^{(0)} \rangle = -\frac{R^2}{2} \{ \beta(1) \gamma(0) + \beta(0) \gamma(1) \}$$

5.

$$\langle a^{(0)} | V_a | b^{(0)} \rangle = -\frac{R^2}{2} \{ \beta(1) \delta(0) + \beta(0) \delta(1) \}$$

$$6. \quad \langle a^{(0)} | V_a | \psi_{ne}(a) \rangle$$

$$= -\sqrt{2} K_{ne} \sum_{p=0}^{n-l-1} \sum_{q=0}^l c_p d_q \frac{R^{l+p+2}}{4} \sum_{s=0}^{l+p-q+1} \sum_{u=0}^q \binom{l+p-q+1}{s} \binom{q}{u} \\ \times \{ \beta(l+p-q-s+u+1) \gamma(s+u) \}$$

$$7. \langle \psi_{ne}(a) | V_b | b^{(a)} \rangle$$

$$= -\sqrt{2} K_{ne} \sum_{p=0}^{n-l-1} \sum_{q=0}^l c_p d_q \frac{R^{p+l+2}}{4} \sum_{s=0}^{l+p-q} \sum_{u=0}^q \binom{l+p-q}{s} \binom{q}{u} \\ \times \left\{ \beta(l+p-q-s+u+1) \delta(s+u) - \beta(l+p-q-s+u) \delta(s+u+1) \right\}$$

$$8. \langle \psi_{ne}(a) | V_a | \psi_{n'l'}(a) \rangle$$

$$= -K_{ne} K_{n'l'} \sum_{p=0}^{n-l-1} \sum_{q=0}^l \sum_{p'=0}^{n'-l'-1} \sum_{q'=0}^{l'} c_p c_{p'} d_q d_{q'} \frac{R^{l+l'+p+p'+2}}{4}$$

$$\times \sum_{s=0}^{l+l'+p+p'-q-q'+1} \sum_{u=0}^{q+q'} \binom{l+p-q+l'+p'-q'+1}{s} \binom{q+q'}{u}$$

$$\times \left\{ \beta(l+l'+p+p'-q-q'-s+u+1) \delta(s+u) \right\}$$

$$9. \langle \psi_{ne}(a) | V_a | \psi_{n'l'}(b) \rangle$$

$$= -K_{ne} K_{n'l'} \sum_{p=0}^{n-l-1} \sum_{q=0}^l \sum_{p'=0}^{n'-l'-1} \sum_{q'=0}^{l'} c_p c_{p'} d_q d_{q'} \frac{R^{p+p'+l+l'+2}}{4}$$

$$\times \sum_{s=0}^{l+p-q+1} \sum_{u=0}^q \sum_{s'=0}^{l'+p'-q'} \sum_{u'=0}^{q'} \binom{l+p-q+1}{s} \binom{q}{u} \binom{l'+p'-q'}{s'} \binom{q'}{u'} (-1)^{s'+u'+q'}$$

$$\times \left\{ \beta(l+p-q-s+u+l'+p'-q'+u'+1) \delta(s+u+s'+u') \right\}$$

REFERENCES

1. J. O. Hirschfelder and R. J. Silbey, WIS-TCI-168A (1966).
2. P. O. Löwdin and H. Shull, Phys. Rev. 101, 1730 (1956).
3. J. O. Hirschfelder and P. O. Löwdin, Mol. Phys. 2, 229 (1959).
4. J. M. Peek, Sandia Corporation Report SC-RR-65-77 (1966).